

## DIRECT DETERMINATION OF OXYGEN IN COAL

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## INTRODUCTION

There are two known methods for the direct determination of oxygen in organic matter:

- 1) Schütze method (1) and modifications (2,3,4,5,6,7,8)
- 2) Neutron activation method (9,10)

The principle of the Schütze method depends on thermal decomposition of the sample in a temperature range of 1000° - 1150°C, in an oxygen free atmosphere of inert gas. The gaseous products of pyrolysis are carried over a layer of carbon black or lampblack at a temperature 1120°C. At this temperature all oxygen containing products are transformed into CO which is quantitatively oxidized using I<sub>2</sub>O<sub>5</sub> to CO<sub>2</sub>. The oxygen content of the sample for analysis can be calculated from the gain in CO<sub>2</sub> measured gravimetrically or from the gain in I<sub>2</sub> measured volumetrically. Instead of oxidizing CO to CO<sub>2</sub> some authors suggest the determination of CO directly using chromatographic analysis. (5)

Using platinum on lampblack (7) or nickel on lampblack (5) as a catalyst, it is possible to decrease the temperature for the quantitative conversion to carbon monoxide of the products of pyrolysis of the sample.

All modifications of the Schütze method for the direct determination of oxygen are based on the thermal decomposition of the sample in an inert gas. This requires a very pure sweeping gas and therefore rather complicated methods for the purification of this gas. In effect this means that the analysis is much more prolonged.

The determination of oxygen using the neutron activation method has been described many times in detail. (10) This method allows the total concentration of oxygen to be determined in both the organic and inorganic constituents of the sample. The advantages of this method are: the short time of duration of the analysis and the fact that this is a non-destructive type of test. On the other hand the equipment for the determination of oxygen using neutron activation analysis is very expensive and the sample must be relatively large.

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Also, if the principal quantity of interest is the oxygen content of the organic matter in the coal, the mineral matter must be removed. This is a rather laborious process.

The recognized methods of determining the oxygen content of coal, based on Schütze (1) Unterzaucher (2) and Burns (8) are slow and require considerable skill to achieve satisfactory levels of accuracy. The method described here is much more rapid and requires considerably less technique.

## EXPERIMENTAL

### Principle of the Method.

A fast and simple method is described for the determination of oxygen in coals. The principle of the method depends on the pyrolysis of a sample at 1050°C in a vacuum, conversion of all oxygen in the pyrolysis products into CO, the determination of the volume of evolved gas and the measurement of the concentration of carbon monoxide in this gas using gas chromatography.

### Apparatus.

The basic part of the determination, which is the pyrolysis and the measurement of the volume of evolved gas is conducted in the apparatus indicated in Figure 1. The part of this apparatus indicated by 1 referred to as the pyrolyser and is used for the pyrolysis of the sample located at a and the evacuation of the catalyst situated at b. As it must withstand relatively high temperature it is made from Vycor glass. The pyrolyser is connected through the unit 2 to a gas burette, capacity 100 ml, by means of heavy rubber tubing. After completion of the pyrolysis, the mercury from the reservoir is introduced into the apparatus through the one-way stopcock c. The pyrolysis is conducted in a hinged tubular electric furnace into which the pyrolyser unit is placed as shown in Figure 2. The additional equipment required for the determination of oxygen includes a vacuum pump and gas chromatograph suitable for the measurement of carbon monoxide. In this investigation a Fisher Partitioner was used with a double column: - hexamethylphosphoramide on Chromosorb P followed by a Linde molecular sieve 13X. Using such a set of columns it was a simple matter to determine whether the conversion process was quantitative or not as the presence of any CO<sub>2</sub> shows that the conversion is incomplete.

The sample for analysis (60 mg - 100 mg) was weighed in the quartz tube 5 whose shape and dimension are presented in Figure 1. With high oxygen content coals such as lignite the sample weight is kept to 60 mg while for anthracite the sample weight is increased to 100 mg.

### Preparation of the Catalyst.

Two hundred gram of lampblack dried at 105°C for 3 hours was mixed in a beaker with a concentrated solution of nickelous nitrate consisting of 991 g  $\text{Ni NO}_3 \cdot 6 \text{H}_2\text{O}$  dissolved in 200 ml of distilled water. The suspension was mixed mechanically and heated to evaporate the water. The heating was stopped when the residue started to solidify. The contents of the beaker were dried for 24 hours at 105°C in an oven. Then, the catalyst was transferred to a Vycor tube swept with argon. The temperature was increased gradually to 1050°C and maintained under these conditions for 5 hours. The catalyst was then cooled and stored in an air-tight container. The particles of the catalyst, 16-60 mesh Tyler, were used for the oxygen determinations.

### Method of Analysis.

Five g of catalyst was introduced into the tube b of the pyrolyser Figure 1. The part a was cleaned carefully to remove all vestiges of catalyst particles and the sample in the quartz tube 5 was introduced into part pyrolyser. The apparatus was assembled, set up on a stand, and evacuated initially for 5 minutes. Then part b of the pyrolyser was inserted into an oven for 30 minutes at 1050°C. Five minutes before the end of this period in which the catalyst was degassed, the apparatus was re-evacuated. At the conclusion of this 5 minute period the tubing b was withdrawn from the furnace and the tubing a was inserted for 10 minutes into a thermostat at a temperature of 70°C to remove traces of moisture from the coal sample. After the tubing b was cold the catalyst was transferred into a by rotating the pyrolyser and the apparatus was disconnected from the vacuum pump using stopcock c. After the pressure dropped to 0.3 mm of Hg, the hinged furnace was opened for some seconds and the tubing a of the apparatus was placed in the furnace as shown in Figure 2 to avoid heating the coal. After some minutes when the temperature stabilized again at 1050°C the furnace was moved very slowly in the direction of the sample. The rate of evolution of the pyrolysis gases from the sample could be observed by eye, and the rate of advance of the furnace was controlled to avoid sudden bursts of gas. The sample was finally advanced to the mid-point of the furnace and retained there for 10 minutes. After this time the pyrolyser was withdrawn from the furnace and 3 to 4 minutes later the mercury from the reservoir was introduced into the apparatus with vibration from 4. The converted pyrolysis gas was displaced into the gas burette. The volume of the gas was measured and the temperature and atmospheric pressure was noted. The concentration of carbon monoxide was determined by withdrawing a sample for gas chromatography.

The concentration of oxygen in analysed sample was calculated from the equation:

$$\%O = \frac{(0.07143)}{G} \left[ \frac{\%CO \cdot P_1 \cdot V_1 \cdot 0.003592}{T_1} - K \right]$$

where: G - weight of sample g ;  $V_1$  - volume of evolved gas (ml)  
(at temperature  $T_1$  pressure  $P_1$ )

$P_1$  - atmospheric pressure mm Hg.

$T_1$  - temperature °K; K - volume of CO ml at temperature 273°K,  
pressure 760 mm of Hg obtained from  
pyrolysis of pure chemical compound not  
containing oxygen.

K is a function of the conditions of analysis such as: temperature,  
time of pyrolysis, method of the preparation  
of catalyst, time and temperature of the  
degasification of catalyst. Consequently,  
to obtain reproducible results it is  
important to adhere strictly to the same  
analytical procedure.

#### Results and Discussion.

The proposed method for the direct determination of oxygen in coal was tested on two standard pure compounds, namely, benzoic acid and acetanilide. Comparative analyses by the neutron activation method were performed on these standards. The results presented in Table 1 show that the proposed method can be considered as a basically suitable analytical procedure for the direct determination of oxygen in many organic compounds. Some caution will have to be used in those cases where the component is known to contain elements that will poison the nickel catalyst.

The establishment of this method for the determination of oxygen in coal required finding the temperature of pyrolysis at which essentially all oxygen from organic matter of coal was evolved from the coke. It was found from the determination of the concentration of oxygen by neutron activation in cokes resulting from the pyrolysis of some coals of different rank demineralized according to Radmacher (11), that the temperature of 1050°C is suitable. This is illustrated in Figure 3. Only in the case of anthracite was the concentration of oxygen in cokes pyrolysed at temperatures of 1050°C and 1100°C relatively high, that is to say approximately 0.9%. At the same time the concentration of ash in this particular anthracite after treatment with hydrochloric acid and hydrofluoric acid was surprisingly high as shown in Table 2, Column 7. So it is assumed that the high concentration of oxygen in cokes from pyrolysis of anthracite at 1050°C and 1100°C is related to the inorganic matter in these cokes. It is worth mentioning that the concentrations of oxygen in both these cokes though heated to different temperatures, i.e., 1050 and 1100°C were the same. Had the oxygen been contained in the organic matter some decrease in concentration should have been observed.

Coals of different rank were analysed before and after removal of the mineral matter using the direct method of determining oxygen. The results are shown in Table 2. Here it is evident that the oxygen content of the demineralized samples are in good agreement with those found by neutron activation analysis.

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TABLE 1. Results from the determination of oxygen in standards

Standards	Oxygen (%)				
	Determined using				Theoretical
	Pyrolysis method	Mean	Neutron activation method	Mean	
1) Benzoic acid	26.3; 26.7; 26.3; 26.0; 26.5; 26.7; 26.2; 26.3; 26.3;	26.4	26.14; 27.16; 27.12; 25.82; 25.54; 25.71;	26.25	26.20
2) Acetanilide	12.2; 11.7; 12.1;	12.0	12.12; 12.24; 11.76;	12.04	11.84

TABLE 2. Oxygen in coal (the results expressed on the dry coal basis)

Sample	Oxygen (%)				Carbon d.a.f.	Ash
	by pyrolysis method	Mean	by neutron activation method	Mean		
1	2	3	4	5	6	7
<u>Bituminous coals</u>						
Moss 3	6.4; 6.9; 6.4; 7.1; 7.1; 6.9;	6.8	8.17; 8.58; 8.84; 8.60;	8.55	82.4	6.73
Moss 3-demineralized	6.6; 6.6; 6.9;	6.7	6.75; 6.73; 6.13;	6.54		0.29
Itmann	4.2; 4.5; 4.0; 4.0;	4.2	6.40; 6.47; 6.68; 6.58;	6.53	85.1	6.30
Itmann-demineralized	4.3; 4.5; 4.2;	4.3	4.26; 4.24; 4.44;	4.31		0.15
<u>Lignites</u>						
Turow-demineralized	24.9; 26.4; 26.4; 26.5;	26.0	26.13; 26.21; 27.77; 25.99; 25.81;	26.38	68.8	0.25
Smogory-demineral- ized	29.9; 31.0; 29.8;	30.2	33.75; 32.38; 36.33; 30.77;	31.62	66.3	0.26
<u>Subbituminous coal</u>						
fresh	-	-	24.30; 24.59;	24.43	75.0	6.24
demineralized	-	-	20.00; 20.29;	20.14		0.11
<u>Anthracite</u>						
fresh	1.8; 2.1	2.0	7.59;	7.59	92.5	11.05
demineralized	2.3; 2.0; 2.2;	2.2	2.66;	2.66		0.91

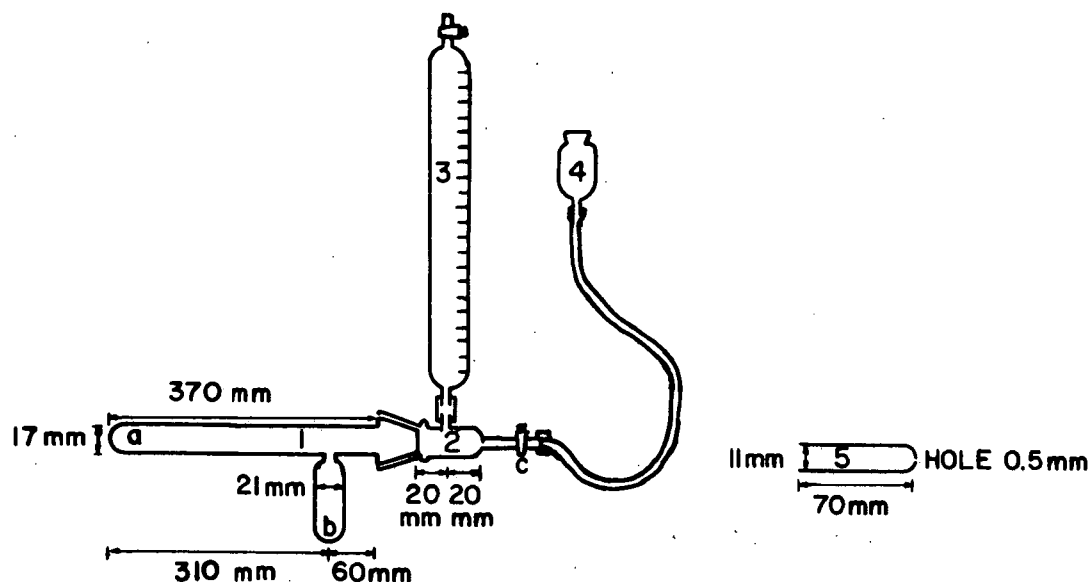


FIGURE 1 - APPARATUS FOR PYROLYSIS CONVERSION AND MEASUREMENT OF VOLUME OF EVOLVED GASES

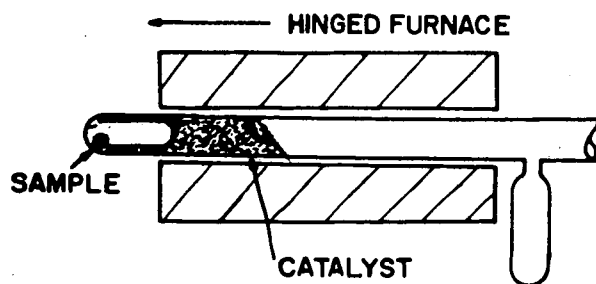


FIGURE 2 - LOCATION OF THE PYROLYSIS TUBING IN OVEN AT THE BEGINING OF EXPERIMENT



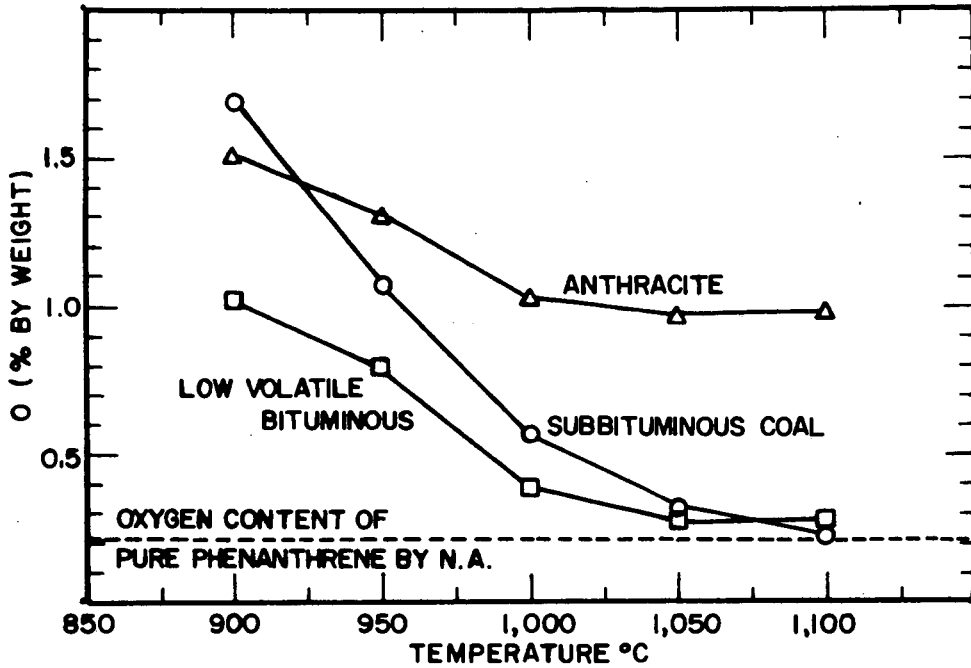


FIGURE 3 - OXYGEN CONTENT BY NEUTRON ACTIVATION OF COKE FROM DEMINERALIZED COAL, PYROLYSED FOR 10 MINUTES AT INDICATED TEMPERATURE